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NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY
AND METHOD FOR MANUFACTURING ELECTROCE PLATES USING IT

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NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY
AND METHOD FOR MANUFACTURING ELECTRODE PLATES USING IT

[Hisui denkaiei niji denchi oyobi koreni mochiiru denkyokuhan no seizo hoho]

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Claims

1. A nonaqueous electrolytic secondary battery, characterized by the fact that in a nonaqueous electrolytic battery equipped with a positive-electrode active material layer which is mainly composed of a Li-transition metal double oxide and has a continuous gap, a negative-electrode active material layer which is mainly composed of graphite and has a continuous gap, and a nonaqueous electrolytic solution which is an organic solvent solution of lithium salt and is filled into the above-mentioned two gaps, the porosity of the above-mentioned

positive-electrode active material layer is 20-29 vol%; and the porosity of the above-mentioned negative-electrode active material layer is 30-45 vol%.

2. A method for manufacturing electrode plates, characterized by the fact that in a method for manufacturing electrode plates for use in the nonaqueous electrolytic secondary battery of Claim 1, a positive-electrode active material is suspended in a solvent and spread and dried as a paste on a positive electrode current collector sheet so that the porosity after spreading and drying may be 60-70 vol%, and rolled to set the porosity of the positive-electrode active material layer to 20-29 vol%; and a negative-electrode active material is suspended in a solvent and spread and dried as a paste on a negative electrode current collector sheet so that the porosity after spreading and drying may be 50-65 vol%, and rolled to set the porosity of the negative-electrode active material layer to 30-45 vol%.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a nonaqueous electrolytic secondary battery such as a lithium secondary battery and a method for manufacturing electrode plates used in it.

[0002]

Prior art

Recently, the formation of portable and cordless electronic equipment for public use has rapidly advanced. Along with this, the demand for a secondary battery which is small and lightweight as a power source for driving and has a high energy density has increased. From such a viewpoint, there is an expectation of a nonaqueous electrolytic secondary battery, especially a lithium secondary battery as a secondary battery with a high voltage and a high energy density, and development is urgent.

[0003]

As positive-electrode active materials of a conventional lithium secondary battery, manganese dioxide, vanadium pentaoxide, titanium disulfide, etc., have been used. The lithium secondary battery has been constituted by a positive electrode using these positive-electrode active materials, a negative electrode using a metal Li, and an organic electrolytic solution. On the other hand, in the secondary battery using the metal Li in the negative electrode, the metal Li precipitated on the negative electrode is deposited in a dendrite shape during charging and breaks through a separator, so that an internal short circuit is caused between the metal and the positive electrode or a side reaction is caused between the metal and the electrolytic solution. Since the

dendrite deposition of the above-mentioned metal Li is significantly increased by charging at a large current and repeating the charge and discharge, a high-speed charge is difficult, and the charge and discharge cycle life is short. Furthermore, there are risks such as severe heat generation or liquid leaks due to the above-mentioned internal short circuit, resulting in a large practical obstacle.

[0004]

Recently, a lithium secondary battery in which a negative-electrode active material mainly composed of a graphite group carbon material, which can reversely intercalate Li, is used without using the metal Li as a negative electrode and a positive-electrode active material mainly composed of a Li-transition double oxide such as LiCoO_2 , which can reversely discharge Li ions, as a positive electrode has been proposed to solve the above-mentioned problems.

[0005]

Problems to be solved by the invention

However, as a result of the review by these inventors, it was clarified that in the above-mentioned lithium secondary battery in which a Li-transition metal double oxide was used as a positive-electrode active material and a graphite group carbon material was used as a negative-electrode active material, the precipitation of the metal Li on the negative electrode during charging was not necessarily sufficient and the charge and discharge cycle characteristics of the lithium secondary battery obtained depended largely on the manufacture conditions of a positive electrode plate and a negative electrode plate.

[0006]

The present invention considers the above-mentioned problems, and its purpose is to provide a nonaqueous electrolytic secondary battery which suppresses the precipitation of a metal Li on a negative electrode during charging and has good charge and discharge cycle characteristics, and a method for manufacturing electrode plates used in it.

[0007]

Means to solve the problems

In order to achieve the above-mentioned purpose, the present invention is characterized by the fact that in a nonaqueous electrolytic battery equipped with a positive-electrode active material layer which is mainly composed of a Li-transition metal double oxide and has a continuous gap, a negative-electrode active material layer which is mainly composed of graphite and has a continuous gap, and a nonaqueous electrolytic solution which is an organic solvent

solution of lithium salt and is filled into the above-mentioned two gaps, the porosity of the above-mentioned positive-electrode active material layer is 20-29 vol%; and the porosity of the above-mentioned negative-electrode active material layer is 30-45 vol%.

[0008]

According to the nonaqueous electrolytic secondary battery of the present invention, since the porosity of the negative-electrode active material is greater than that of the positive-electrode active material, the volume rate of an electrolytic solution in the negative-electrode active material layer is greater than that of the positive-electrode active material, so that the mobility of Li ions in the negative-electrode active material layer is greater than that of the positive-electrode active material layer. Therefore, in the negative-electrode active material layer during charging, since the Li ions being supplied into the electrolytic solution from the positive electrode are smoothly intercalated into the negative-electrode active material without difficulty, the metal Li can be suppressed from being locally precipitated in the negative electrode. Then, as shown in Figures 2 and 4, when the porosity of the positive-electrode active material layer is in a range of 20-29 vol% and the porosity of the negative-electrode active material layer is in a range of 30-45 vol%, the size relationship between the balance of the amount of each active material in the positive electrode and the negative electrode and the mobility of the Li ions in each active material layer is appropriately maintained, so that a nonaqueous electrolytic secondary battery with good charge and discharge cycle characteristics can be obtained.

[0009]

If the porosity of the positive-electrode active material layer is less than 20 vol%, the volume rate of the electrolytic solution in the positive-electrode active material layer is decreased, and the mobility of the Li ions in the positive-electrode active material layer is lowered, so that the internal resistance is increased during discharging, which is not preferable. If the porosity of the positive-electrode active material layer is more than 29 vol%, the porosity of the positive electrode active material is decreased, so that the battery capacity per unit volume is lowered, which is not preferable. Also, if the porosity of the negative electrode active material layer is less than 30 vol%, the volume rate of the electrolytic solution in the negative electrode active material layer is decreased, and the mobility of the Li ions in the negative electrode active material layer is lowered, so that the metal Li is locally precipitated in the negative electrode and deposited in a dendrite shape, which is not preferable. If the porosity of the negative electrode active material layer is greater than 45 vol%, the packing rate of the negative-electrode active

material is decreased, so that the electric conductivity in the negative-electrode active material is decreased and the battery capacity per unit volume is lowered, which is not preferable.

[0010]

In the method for manufacturing electrode plates for use in the above-mentioned nonaqueous secondary battery, a positive-electrode active material is suspended in a solvent and spread and dried as a paste on a positive electrode current collector sheet so that the porosity after spreading and drying may be 60-70 vol%, and rolled to set the porosity of the positive-electrode active material layer to 20-29 vol%, and a negative-electrode active material is suspended in a solvent and spread and dried as a paste on a negative electrode current collector sheet so that the porosity after spreading and drying may be 50-65 vol%, and rolled to set the porosity of the negative-electrode active material layer to 30-45 vol%. Thus, the electrode plates being used in the above-mentioned nonaqueous electrolytic secondary battery can be manufactured as long sheets suitable for an integrated automation of spreading, drying, and rolling without trouble. As shown in Figures 3 and 5, when the porosity after spreading and drying of the positive-electrode active material is in a range of 60-70 vol% and the porosity after spreading and drying of the negative-electrode active material is in a range of 50-65 vol%, a nonaqueous electrolytic secondary battery with good charge and discharge cycle characteristics can be obtained.

[0011]

If the porosity after spreading and drying of the positive-electrode active material is less than 60 vol%, the rolling rate is decreased, the electrical contact degree of the positive-electrode active material and the positive electrode plate is small, and the electric conductivity in the positive-electrode active material layer is lowered, so that the internal resistance is increased during discharging, which is not preferable. If the porosity after spreading and drying of the positive-electrode active material is more than 70 vol%, large voids are nonuniformly generated in the positive-electrode active material layer, and the distribution irregularity of the positive-electrode active material remains even after rolling, which is not preferable. Also, if the porosity of spreading and drying of the negative-electrode active material layer is less than 50 vol%, the rolling rate is decreased, and the electrical contact degree of the negative-electrode active material and the negative electrode plate is small, so that the electric conductivity in the negative-electrode active material layer is lowered, which is not preferable. If the porosity after spreading and drying of the negative-electrode active material is more than 65 vol%, the rolling rate is increased, and the basal plane of the graphite as a main component of the negative is oriented parallel with the negative electrode plate surface, and the mobility of the Li ions in the

negative-electrode active material layer is lowered, so that the metal Li is locally precipitated in the negative electrode during charging, which is not preferable.

[0012]

Embodiment of the invention

An embodiment of the present invention is explained below based on the figures.

[0013]

An embodiment of the nonaqueous electrolytic secondary battery of the present invention is a cylindrical lithium secondary battery as shown in Figure 1 and consists of an electrode plate group, an electrolytic solution, and a battery case for housing them.

[0014]

The electrode plate group consists of a sheet-shaped positive electrode plate 1, a sheet-shaped negative electrode plate 3, a sheet-shaped separator 5 for insulation between the positive electrode plate 1 and the negative electrode plate 3, a positive electrode lead 2, a negative electrode lead 4, an upper insulating plate 6, and a lower insulating plate 7. In the positive electrode plate 1, positive-electrode active material layers are spread and formed on both surfaces of an aluminum foil so that the porosity may be 20-29 vol%. In the negative electrode plate 3, negative-electrode active material layers are spread and formed on both surfaces of a copper foil so that the porosity may be 30-45 vol%. These positive electrode plate 1 and negative electrode plate 3 are superposed via the separator 5 made of a porous polypropylene film, wound in a spiral shape, and reliably housed in the cylindrical battery case.

[0015]

The electrolytic solution is composed of a nonaqueous electrolytic solution in which lithium perchlorate is dissolved at a concentration of 1 mol/L in an equal volume mixed solvent of ethylene carbonate and propylene carbonate. The nonaqueous electrolytic solution is housed in the battery case, also filled into the continuous gaps in the positive-electrode active material layer and the negative-electrode active material layer, and moves Li ions between the positive electrode plate 1 and the negative electrode plate 3 through fine holes of the porous separator 5 in a battery reaction.

[0016]

The battery case consists of a base body 8 obtained by deep-drawing a stainless steel plate with an organic electrolytic solution resistance, a sealing plate 10 in which a safety valve

11 is installed, and an insulating gasket 9 for an insulation and a gas seal between the sealing plate 10 being an external terminal of the positive electrode and the case body 8 being an external terminal of the negative electrode.

[0017]

An embodiment of the method for manufacturing electrode plates being used in the above-mentioned nonaqueous electrolytic secondary battery of the present invention is explained below.

[0018]

As the positive electrode plate 1, as shown in Table I, one of positive electrode plate samples A-L in which the porosity of the active material layer and the porosity after spreading and drying the active material were changed by controlling various manufacture conditions was obtained. Specifically, 90 wt% LiCoO_2 powder obtained by mixing Li_2CO_3 and CoCO_3 and baking it at 900°C for 10 h, 3 wt% acetylene black, and 7 wt% fluororesin adhesive were mixed, and this mixture was suspended in an aqueous solution of 1 wt% carboxymethyl cellulose, so that positive-electrode active material pastes with various concentrations (water contents) were obtained. Then, these positive-electrode active material pastes were spread and dried at various thicknesses on both surfaces of an aluminum foil at a thickness of 0.02 mm, so that spread positive electrode layers with various porosities in accordance with the concentrations of the positive-electrode active material pastes used were obtained. Finally, they were rolled at a thickness of 0.18 mm and tailored, so that positive electrode plate samples A-L with a width of 40 mm and a length of 350 mm were obtained. Table 1 shows the apparent density and the spreading thickness corresponding to the porosity, and in an actual manufacturing process, these apparent density and spreading thickness are convenient for controlling the conditions.

[0019]

As the negative electrode plate, as shown in Table II, 12 kinds of negative electrode plate samples M-Y in which the porosity of the active material layer and the porosity after spreading and drying of the active material were changed by controlling various manufacture conditions. Specifically, a coke being formed by dry-distilling a coal at high temperature was crushed at an average particle diameter of $6.0\text{ }\mu\text{m}$ by a jet mill and baked at $2,800^\circ\text{C}$, so that a graphite was formed. The specific surface of the graphite powder obtained was $5.0\text{ m}^2/\text{g}$. 90 wt% of the graphite powder and 10 wt% fluororesin group binder were mixed, and this mixture was suspended in an aqueous solution of 1 wt% carboxymethyl cellulose, so that negative-electrode active material pastes with various concentrations (water contents) were obtained. Then, these

negative-electrode active material pastes were spread and dried at various thicknesses on both surfaces of a copper foil with a thickness of 0.02 mm, so that spread negative electrode layers with various porosities in accordance with the concentrations of the negative-electrode active material pastes used were obtained. Finally, they were rolled at a thickness of 0.19 mm and tailored, so that negative electrode plate samples M-Y with a width of 40 mm and a length of 420 mm were obtained. Table 2 also shows the apparent density and the spreading thickness corresponding to the porosity, and in an actual manufacturing process, the apparent density and spreading thickness are convenient for controlling the conditions.

[0020]

(Table 1)

8

①	正極板試料	単位	A	B	C	D	E	F	G	H	J	K	L
②	ペースト含水率	wt%	63	57	50	44	38	50					
③	活物質塗布厚み	(mm)	0.55	0.47	0.41	0.36	0.32	0.38	0.39	0.41	0.43	0.44	0.45
④	活物質の塗布乾燥後の空隙率	vol%	75	70	65	60	55	65					
	(みかけ密度)	(g/cm ³)	1.2	1.4	1.6	1.8	2.0	1.6					
⑤	活物質層の厚み	(mm)	0.16										
⑥	活物質層の空隙率	vol%	26					35	32	29	23	20	17
	(みかけ密度)	(g/cm ³)	3.5					3.2	3.3	3.4	3.6	3.7	3.8
⑦	圧延率	%	70	64	59	53	47	56	57	58	61	62	63

- Key: 1 Positive electrode plate sample
 2 Paste content
 3 Active material spreading thickness
 4 Porosity after spreading and drying of active material (apparent density)
 5 Thickness of active material layer
 6 Porosity of active material layer (apparent density)
 7 Rolling rate
 8 Unit

[0021]
(Table 2)

2)

①	負極板試料	単位	M	N	P	Q	R	S	T	U	V	W	X	Y
②	ペースト含水率	wt%	70	66	60	55	50	43	35	50				
③	活性物質塗布厚み	(μm)	0.30	0.33	0.29	0.25	0.23	0.21	0.19	0.21	0.23	0.27	0.29	0.31
④	活性物質の塗布乾燥後の空隙率 (みかけ密度)	vol% (g/cm^3)	75 0.6	70 0.7	65 0.8	60 0.9	55 1.0	50 1.1	45 1.2	55 1.0				
⑤	活性物質層の厚み	(μm)	0.17											
⑥	活性物質層の空隙率 (みかけ密度)	vol% (g/cm^3)	45 1.2							50 1.1	40 1.3	35 1.4	30 1.5	25 1.6
⑦	圧延率	%	54	45	36	27	18	9	0	10	21	31	37	41

- Key:
- 1 Positive electrode plate sample
 - 2 Paste content
 - 3 Active material spreading thickness
 - 4 Porosity after spreading and drying of active material (apparent density)
 - 5 Thickness of active material layer
 - 6 Porosity of active material layer (apparent density)
 - 7 Rolling rate
 - 8 Unit

[0022]

The above-mentioned positive electrode plate samples A-L and negative electrode plate samples M-Y were variously combined, wound in a spiral shape via the separator made of a porous polypropylene film with a length of 0.025 mm, a width of 46 mm, and a length of 900 mm, and assembled into a battery case with a diameter of 17 mm and a height of 50 mm, and the above-mentioned nonaqueous electrolytic solution was filled into it. Using these combinations of the positive electrode plates 1 and the negative electrode plates 3 under various manufacturing conditions, lithium secondary batteries were obtained. The evaluation results of the charge and discharge cycle characteristics of the lithium secondary batteries obtained are shown in Figures 2-6.

[0023]

As one method for evaluating the charge and discharge cycle characteristics, charging was carried out for 2 h while limiting the initial charge current to 500 mA and the upper charge voltage to 4.2 V at an environmental temperature of 20°C, and after holding for 30 min,

discharging was carried out at a constant current of 720 mA until the final voltage reached 3 V. After repeating this charge and discharge cycle 500 times, the discharge capacity was measured, and as shown in Figures 2-5, the variables of each manufacturing condition were adopted and plotted on the abscissa.

[0024]

Figure 2 shows the relationship between the porosity of the positive-electrode active material layer and the charge and discharge cycle characteristics. The porosity after spreading and drying of the positive-electrode active material before rolling was set to 65 vol%, and all the negative electrode plates being combined were assumed as the negative electrode plate sample R. As shown in Figure 2, good charge and discharge cycle characteristics were obtained when the porosity of the positive-electrode active material layer was in a range of 20-29 vol% (positive-electrode plate samples H, C, J, and K).

[0025]

Figure 3 shows the relationship between the porosity after spreading and drying of the positive-electrode active material. The porosity after spreading and drying of the positive-electrode active material after rolling was set to 26 vol%, and all the negative electrode plates being combined were assumed as the negative electrode plate sample R. As shown in Figure 3, good charge and discharge cycle characteristics were obtained when the porosity after spreading and drying of the positive-electrode active material was in a range of 60-75 vol% (positive-electrode plate samples B, C, and D).

[0026]

Figure 4 shows the relationship between the porosity of the negative-electrode active material layer and the charge and discharge cycle characteristics. The porosity after spreading and drying of the negative-electrode active material before rolling was set to 55 vol%, and all the positive electrode plates being combined were assumed as the positive electrode plate sample C. As shown in Figure 4, good charge and discharge cycle characteristics were obtained when the porosity of the negative-electrode active material layer was in a range of 30-45 vol% (negative-electrode plate samples R, V, W, and X).

[0027]

Figure 5 shows the relationship between the porosity after spreading and drying of the negative-electrode active material. The porosity after spreading and drying of the negative-electrode active material after rolling was set to 45 vol%, and all the positive electrode

plates being combined were assumed as the positive electrode plate sample C. As shown in Figure 5, good charge and discharge cycle characteristics were obtained when the porosity after spreading and drying of the negative-electrode active material was in a range of 50-65 vol% (negative-electrode plate samples P, Q, R, and S). As another method for evaluating the charge and discharge cycle characteristics, the same charge and discharge cycle conditions as the above-mentioned conditions were repeated for each of lithium secondary batteries based on four kinds of representative combinations, and the discharge capacity was measured for each cycle. As shown in Figure 6, the number of cycles was adopted and plotted on the abscissa. Specifically, four kinds of combinations of the positive electrode plate samples and the negative electrode plate samples, that is, J-V, J-Y, F-V, and F-Y were evaluated. As shown in Figure 6, it is understood that when the negative electrode plate sample V with a large porosity (a porosity of 40 vol%) and the positive electrode plate sample J with a small porosity (a porosity of 23 vol%) are used, the initial discharge capacity is large, and the decrease of the discharge capacity to the increase of the number of cycle is small, that is, the charge and discharge cycle characteristics are good. When the negative electrode plate sample Y with a small porosity (a porosity of 25 vol%) is used, the decrease of the discharge capacity to the increase of the number of cycle is large, which is not preferable, and when the positive electrode plate sample F with a large porosity (a porosity of 35 vol%) is used, the initial discharge capacity is small, which is not preferable.

[0028]

From these facts and the above-mentioned results of Figures 2 and 4, it is understood that though the porosity of the active material layer of the negative electrode plate is large and the porosity of the active material layer of the positive electrode plate is small, the charge and discharge cycle characteristics are good. Needless to say, if the porosity of the active material layer of the negative electrode plate is significantly increased, since the packing rate of the negative-electrode active material is decreased, the electric conductivity in the negative-electrode active material is lowered, and the battery capacity per unit volume of the battery is lowered, which is not preferable. Also, if the porosity of the active material layer of the positive electrode plate is significantly decreased, the mobility of Li ions in the positive electrode active material layer is lowered, which is not preferable.

[0029]

Also, from the above-mentioned results of Figures 3 and 5, it is understood that good charge and discharge cycle characteristics can be obtained by respectively rolling the positive electrode plate and the negative electrode plate at an appropriate rolling rate. In particular, for the

positive-electrode active material mainly composed of a LiCoO_2 powder with an inferior electric conductivity in itself, only when an electroconductive material is added and rolling is applied to some degree is a sufficient electric conductivity created, so that good charge and discharge cycle characteristics are obtained.

[0030]

Effect of the invention

According to the nonaqueous electrolytic secondary battery of the present invention, since the porosity of the negative-electrode active material layer is greater than that of the positive-electrode active material, the volume rate of an electrolytic solution in the negative-electrode active material is greater than that of the positive-electrode active material, so that the mobility of Li ions in the negative-electrode active material layer is greater than that of the positive-electrode active material layer. Therefore, in the negative-electrode active material layer during charging, since the Li ions being supplied into the electrolytic solution from the positive electrode are smoothly intercalated into the negative-electrode active material without difficulty, the metal Li can be suppressed from being locally precipitated in the negative electrode. Then, when the porosity of the positive-electrode active material layer is in a range of 20-29 vol% and the porosity of the negative-electrode active material layer is in a range of 30-45 vol%, the size relationship between the balance of the amount of each active material in the positive electrode and the negative electrode and the mobility of the Li ions in each active material layer is appropriately held, so that a nonaqueous electrolytic secondary battery with good charge and discharge cycle characteristics can be obtained.

Brief description of the figures

Figure 1 is a cross section showing an embodiment of the nonaqueous electrolytic secondary battery of the present invention.

Figure 2 shows the relationship between the porosity of a positive-electrode active material layer and the charge and discharge cycle characteristics.

Figure 3 shows the relationship between the porosity after spreading and drying of a positive-electrode active material and the charge and discharge cycle characteristics.

Figure 4 shows the relationship between the porosity of a negative-electrode active material layer and the charge and discharge cycle characteristics.

Figure 5 shows the relationship between the porosity after spreading and drying of a negative-electrode active material and the charge and discharge cycle characteristics.

Figure 6 shows the charge and discharge cycle characteristics of an application example of four kinds of representative nonaqueous electrolytic secondary batteries.

Explanation of reference numerals

- 1 Positive electrode plate
- 2 Negative electrode plate

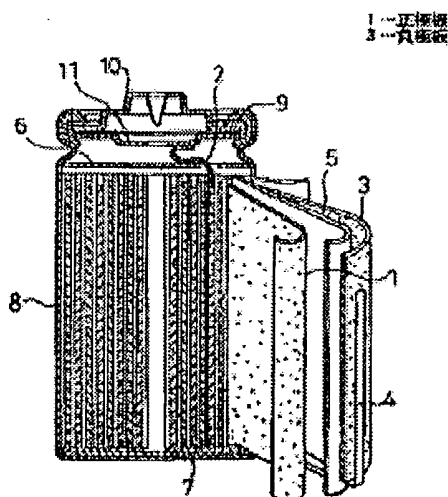


Figure 1

- Legend:
- 1 Positive electrode plate
 - 2 Negative electrode plate

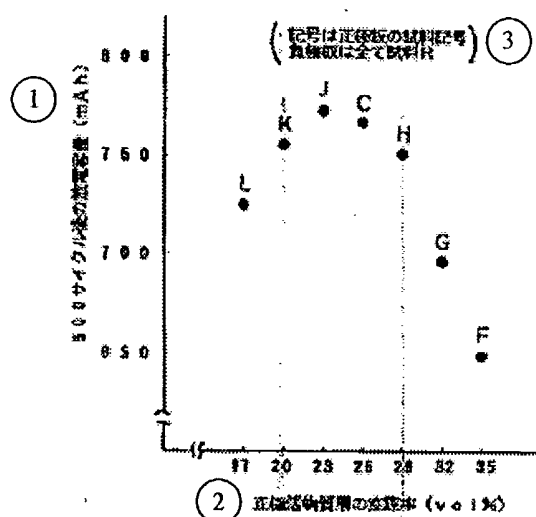


Figure 2

- Key:
- 1 Discharge capacity after 500 cycles (mAh)
 - 2 Porosity of positive-electrode active material layer (vol%)
 - 3 The symbols are positive electrode plate sample symbols. All the negative electrode plates are the sample R.

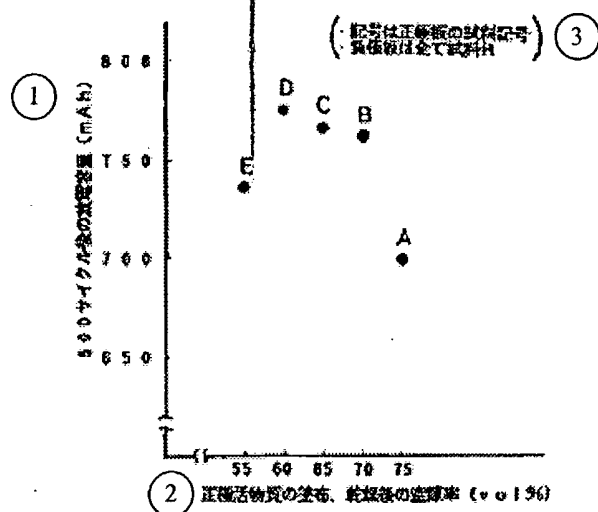


Figure 3

- Key:
- 1 Discharge capacity after 500 cycles (mAh)
 - 2 Porosity after spreading and drying of positive-electrode active material layer (vol%)
 - 3 The symbols are positive electrode plate sample symbols. All the negative electrode plates are the sample R.

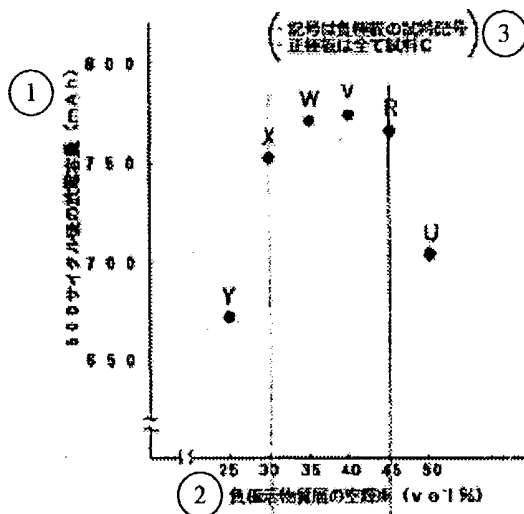


Figure 4

- Key:
- 1 Discharge capacity after 500 cycles (mAh)
 - 2 Porosity of negative-electrode active material layer (vol%)
 - 3 The symbols are negative electrode plate sample symbols. All the positive electrode plates are the sample C.

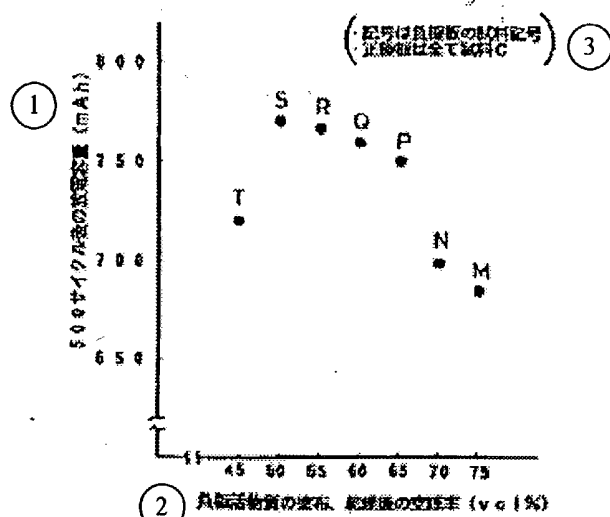


Figure 5

- Key: 1 Discharge capacity after 500 cycles (mAh)
 2 Porosity after spreading and drying of negative-electrode active material layer (vol%)
 3 The symbols are negative electrode plate sample symbols. All the positive electrode plates are the sample C.

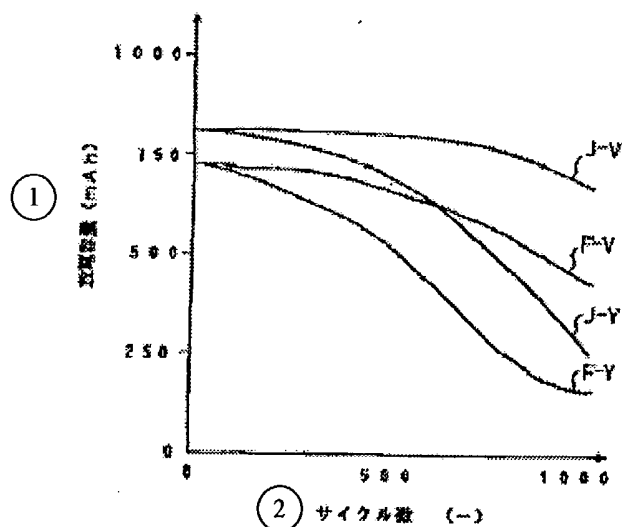


Figure 6

- Key: 1 Discharge capacity (mAh)
 2 Number of cycles (-)